Synthesis of La$_{1-x}$Ca$_x$MnO$_3$ nanowires by a sol–gel process

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Abstract

La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) nanowires were prepared using a simple sol–gel process and nano-channel alumina (NCA). X-ray diffraction (XRD) and selected-area electron diffraction (SAED) indicate that the nanowires are of monoclinic perovskite structure. Transmission electron microscopy (TEM) shows that the diameters of nanowires are around 30 nm. Furthermore, high-resolution TEM reveals a clear lattice image of {021} planes in a LCMO nanowire. It can be expected that the method presented in this Letter is also appropriate for the preparation of nanowires of other mono-component or multi-component oxides.

1. Introduction

Since the discovery of carbon nanotube in the early 1990s [1], quasi one-dimensional materials have attracted much attention due to their significant technological implications. Plenty of efforts have been expended on the synthesis of nanoscale materials of various elements and compounds such as Si [2–6], Ge [7,8], GaN [9], SiC [10,11], ZnO [12], CdS [13], and so on. The techniques involved in the synthesis of nanoscale materials can be generally catalogued into chemical and physical routes. Regarding the template for the growth of nanoscale materials (e.g., diamond nanocylinders and silicon nanowires), the nano-channel alumina (NCA) has been proved desirable and flexible [14,15]. Up to now, the synthesis of nanowires of multi-component oxides is still a challenging issue. In this Letter, we select perovskite-like La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) as a subject, which is well known as an important giant magnetoresistance (GMR) material thus received intensive investigations over the years [16–18]. In the present work, the NCA substrate and a sol–gel process were employed to prepare LCMO nanowires.

2. Experimental

A pure Al plate (99.99%) was annealed at 500 °C for 2 h in vacuum to form texture, then degreased in acetone. Subsequently, it was anodized at 16 °C in oxalic acid solution at a constant voltage of 42 V for 3 h. As a result, an anodic oxide layer was formed. The top part of this layer was disorderly, which was removed in a mixture of phosphoric acid and chromic acid. After this
removal, the textured Al plate was anodized again for 10 h under the conditions identical to those for the first anodizing step. Then the backside Al layer of the specimen was removed in a saturated CuCl₂ solution. The bottom part of the membrane was removed by exposure to phosphoric acid at 30 °C for 90 min, finally, the anodized aluminum oxide (AAO) in porous structure was formed and dried at 30 °C. Because the diameters of pores (channels) of AAO lie in several tens of nanometers range, hereafter, the AAO is referred to NCA.

According to a nominal composition of La₀.₈Ca₀.₂MnO₃ (LCMO), stoichiometric amounts of La₂O₃ and CaCO₃ were dissolved in hot nitric acid, then measured amount of Mn(NO₃)₂ solution was introduced under stirring to form a homogeneous mixed nitrate solution which was then diluted by deionized water to a pH level of about 2.5. The NCA template was put into a culture dish containing a proper amount of the above-mentioned mixed nitrate solution. Then the culture dish was kept at 80 °C for gradual removal of the water in solution. Due to the hydrolysis of metal cations (La³⁺, Ca²⁺, Mn²⁺) present in the solution, a transparent viscous sol was formed upon evaporation of the water. The viscosity of sol was dependent on the extent of water evaporation. In the experiment, the NCA template in which the sol was incorporated into the channels was taken out of the sol when the sol could not flow freely, then put into a tube furnace. The temperature of tube furnace was ramped from room temperature to 400 °C with a rate of 2 °C/min and kept at this temperature for 1 h, then ramped to 800 °C with a rate of 10 °C/min. After firing at 800 °C for 2 h, the power of furnace was off and the NCA template was taken out of the tube furnace until the temperature decreased to about 100 °C.

The synthesized material with a nominal composition of La₀.₈Ca₀.₂MnO₃ confined in the NCA’s channel and the supporting NCA template were ground into powders for the examination of phase on a large scale by powder X-ray diffraction (XRD). Transmission electron microscopy (TEM) observation was performed with a Philips CM200 microscope operated at 200 kV. To prepare the samples for TEM observation, the LCMO nanowires were detached from NCA template by dissolving of AAO in 1 M NaOH solution at 60 °C for 1 h with ultrasonic stirring, then a small drop of the solution was dipped onto a Cu grid covered with a carbon film.

3. Results and discussion

Fig. 1 shows the XRD spectrum for the powders. As marked in the figure, the spectrum consists of two sets of peaks. According to the standard JCPDS cards, one set corresponds to the monoclinic perovskite structure with a nominal composition of La₀.₈Ca₀.₂MnO₃, and the other to γ-Al₂O₃. Therefore, the single-phase perovskite LCMO can be achieved by sol–gel process at an extraordinary low temperature of 800 °C, while, it is generally obtained at elevated temperatures (e.g., 1100–1300 °C) by the standard solid-state reaction technique [16]. The mixture of the constituents of LCMO at molecular (atomic) level in the sol–gel process is the most important factor for the reduced firing temperature.

The TEM micrographs in Fig. 2 show the typical morphology of LCMO nanowires. Fig. 2a shows a typical LCMO nanowire with a diameter of about 30 nm. Interestingly, Fig. 2b illustrates an array of nanowires, also having nearly the same diameter of about 30 nm. Although the lengths of nanowires are much less than 1 μm, it does not
mean that the nanowires are only so short, because during the preparation of samples for TEM observation, the nanowires were easily broken by the ultrasonic stirring. Theoretically speaking, the lengths of nanowires should be in the order of those of NCA’s channels. The inset in Fig. 2b shows the corresponding selected-area electron diffraction (SAED) pattern, in which three diffraction rings match well with the (202), (222), and (422) planes for LCMO with monoclinic perovskite structure. It should be noted that the diffraction rings are discontinuous and consist of rather sharp spots, which indicates that the nanowires are well crystallized. Fig. 3 shows the high-resolution TEM (HRTEM) image of a nanowire. The distance between the parallel fringes is about 0.347 nm, corresponding to the spacing of \(\{021\}\) planes of LCMO with monoclinic perovskite structure. Overall, the results of XRD, SAED, and HRTEM should be considered to be consistent, although XRD pattern reveals much more crystal planes than SAED pattern does, and HRTEM only shows a lattice image of \(\{021\}\) planes. The differences among the results of XRD, SAED, and HRTEM are understandable. In principle, compared with SAED, XRD is relatively macroscopic, while, HRTEM addresses much more microscopic field.

The growth mechanism of LCMO nanowires is proposed as follows. Firstly, the NCA’s channels offer the space confinement across the diameter, which is essential for the growth of nanowires. Secondly, the constituents of LCMO in the form of solution enable themselves to readily enter into the NCA’s channels. Along with the evaporation
of solution, condensation of the hydrolyzed species of metal ions present in aqueous solution will occur, which leads to formation of a hydroxo bridge $\text{M-OH-M}$ or an oxo bridge $\text{M-O-M}$, depending upon pH of the solution [19]. These condensation reactions can be followed by successive associations, leading to polymerization and consequently viscous sol. Obviously, the formation of viscous sol facilitates the conservation of precursor of LCMO within the NCA’s channel at the utmost when the NCA template is taken out of the sol. During the temperature ramping in the tube furnace, the sol within the NCA’s channels would change into gel and further spontaneously combust with liberating vapors such as $\text{H}_2\text{O}$, $\text{NO}_x$. At ever-higher temperatures, the solid-state reaction would occur among the remained constituent metallic oxides for LCMO, which have been sufficiently mixed as a result of sol–gel process. Ultimately, it leads to LCMO with monoclinic perovskite structure. It should be pointed out that the diameters of the resulting LCMO nanowires are smaller than those of NCA’s channels, because of the dehydration and gas liberation during the sol–gel process as mentioned above.

4. Conclusions

In summary, we have successfully achieved nanowires of LCMO with monoclinic perovskite structure using sol–gel process and NCA template. The basic idea behind this method is to use NCA’s channels for space confinement across the diameter, and moreover, to employ sol–gel process for low temperature synthesis of LCMO within the NCA’s channels. XRD and SAED indicated that the nanowires of LCMO with monoclinic perovskite structure could be formed at 800 °C using sol–gel process. TEM revealed that the LCMO nanowires were nearly uniform in size with a diameter of about 30 nm. Furthermore, HRTEM illustrated a clear lattice image of $\{021\}$ planes. However, the characterization for properties of LCMO nanowires is still a difficult and challenging issue for the time being. By the way, it is worth pointing out that although the method presented in this work focuses on the LCMO, it is considered to be feasible for processing nanowires of other mono-component and multi-component oxides.

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References